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Study of *carbon nanodots* from water hyacinth (*Eichornia crassipes*) to degrade textiles dyes of skycion yellow HE-4R

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Abstract. The textile industry and textile products are one of the fastest growing industries in Indonesia. On the other hands the development of textile industry has a negative impact on the environment because it contains harmful chemical compounds. One step to degrade the present of dye compound in textile's waste water is using carbon nanodot (C-Dots). In this research, C-Dots was produced from water hyacinth by microwave assisted method. NaOH and NaOCl₂ were used to remove lignin and hemicellulose while a direct heating method with a furnace was used for carbonation process. The optimum condition of C-Dots concentration to degrade the azo dye were determined by observing the absorbance parameter and chemical oxygen demand (COD) in the textile's waste water. The highest absorbance reduction of the azo dye, Skycion Yellow HE 4R, 10 ppm at wavelength 700nm came from solution with C-Dots with ratio 4:1 (gram C-Dots to liter of waste water). From this result, it can be concluded that C-Dots produced from Water Hyacinth can be used to degrade azo dyes in textile waste water.

Keywords: Carbon Nanodots; Water Hyacinth; *Eichornia Crassipes*; Textiles Dyes

1. Introduction

Azo dyes are the most widely available compound in textile waste, with a presence of more than 50% [1]. Azo dye waste is a representation of a carcinogenic class of organic pollutants. Conventional wastewater treatment methods, which refer to aerobic biodegradation, have a strong efficiency against reactive dyes and other anionic dyes. Biodegradation is very suitable for conventional waste treatment but less effective in removing dyestuffs. In addition, it requires high costs and less effective for processing with large amounts of dyes [2].

Among the various methods of dye removal, adsorption is the best choice because it can eliminate various types of dyes. The right designed adsorption system will produce good quality output. Most commercial waste water treatment processes utilize activated carbon as adsorption agent to remove dyestuffs from waste water because it has excellent adsorption capability.

Activated carbon is a carbon material with open pores that can adsorb small molecules. The advantage of using activated carbon in waste water treatment is the effectivity of absorption ability in removing pollutants from waste water, but it can also adsorb metals such as iron, copper, nickel, and can eliminate odours, colours and flavours contained in wastewater. In addition, activated carbon has high quality products, the process is also very economical, but the dye in adsorption process is absorbed by carbon only, it makes the activated carbon needs to regenerated when the carbon already at the saturated condition. On the other hands, the regeneration process produce wastewater contains dyes, because the adsorption is not degraded into a simpler element.

This research studied the manufacture of as materials that have photoluminous properties and analyzed the application of C-Dots to degrade textile dyes of Skycion Yellow HE 4R by varying the C-Dots concentrations and aging time.



2. Methods

2.1. Raw Material and chemical preparation

Water hyacinth (*Eichornia Crassipes*) from Jatiluhur Purwakarta, West Java was used as raw material to produce C-Dots. Skycion Yellow HE 4R was used as colouring agent. NaOH and NaClO₂ technical grade from Sigma-Aldric were used as chemical agent in this research.

2.2. C-Dots Production

Preparation of C-Dots begins from making small of 40 gram of the stems water hyacinth (*Eichornia crassipes*) plants with size up to 1-3 mm using blades and blenders and then it was dried in the oven at 105°C for 2 hours. After that, delignification and extraction process of cellulose were carried out by in situ process using 4% NaOH solution at 70°C for 2 hours. The residue from extraction and delignification process was separated from its filtrate and 3% NaClO₂ solution was added into the residue for bleaching process at 70°C for 3 hours [3]. The products from bleaching process was filtered and the residue was washed till the pH of 7 using aqueous and dried in the oven at 70°C for 2 hours to produce white dry cellulose. Then 0.75 gram of white dry cellulose was carbonized using a furnace at temperature 300°C for 150 minutes to obtain carbon black. To produce C-Dots, carbon black in aqueous was heated using microwave at temperature 68°C for 40 minutes, then analysed. [4].

2.3. Characterization

The characteristic of C-Dots product was analysed using Transmission Electron Microscope (TEM) Hitachi SU 3500 with Edax Octane Pro, Fourier transform infrared (FT-IR), 500 with KBr disc. Each spectrum was recorded from 4000 to 400 cm⁻¹ using 12 scans at a resolution of 4 cm⁻¹.

2.4. Performance Test

Performance test was determined on 10 ppm Skycion Yellow HE 4R solution. Typically, one liter of 10 ppm of Skycion Yellow HE-4R solution (in de-ionized water) was prepared. Then 4, 8, 12, 16 gram of C-Dots was added to the solution. After that, the absorbance of C-Dots and dye solution were analysed using Shimadzu UV-Vis spectrophotometry, Japan.

3. Result and Discussion

Extraction process and bleaching process which aims to separate lignose from lignocellulose. The components of lignocellulose compartment can be separated, while the bleaching process is carried out after the delignification process, this is done because the cellulose still produces the remaining of lignin. In addition, the bleaching process is intended to increase the brightness and purity of cellulose and reduce the content of resin. On the other things it can reduce the purity of cellulose [5].

The extraction process is carried out using a microwave to induce carbon dissolved in water, it produces C-Dots which are free of aggregates [6], in this condition the microwave will vibrate the carbon dissolved in the water and makes carbon chains undergo rearrangement without reduce a lot of water content in it [5].

The results of the dispersed C-Dots generated from the 4:1, 8:1, 12:1 and 16: 1 (w /v) ratio can be seen in Fig. 1. The brownish solutions which obtained by filtering process shows the existence of C-Dots dispersed in the solution.

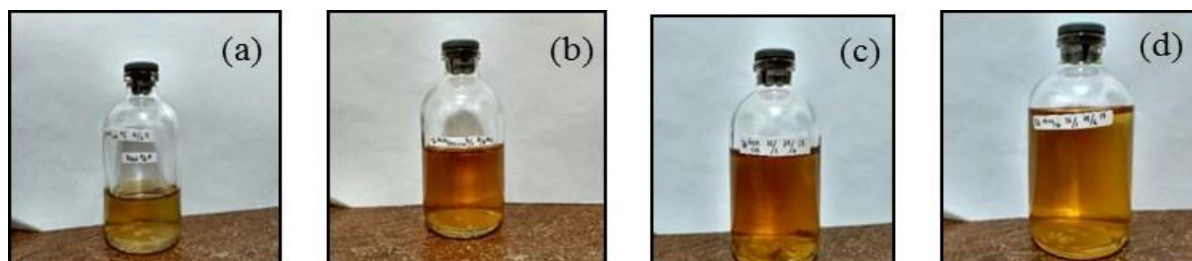


Figure 1. (a) C-Dots Ratio 4:1 (b) C-Dots Ratio 8:1 (c) C-Dots Ratio 12:1, and (d) C-Dots Ratio 16:1 (w/v).

The dispersion of C-Dots obtained from four variations of the ratio produce different colour as shown in Fig. 1. The higher ratio presents darker colour of solution. This is because the more carbon dissolved in the water in the extraction process, the more nano-sized particles are dispersed in the water. The brown colour of the resulting filtrate shows the presence of finely dispersed carbon products. Fine dispersion will be formed if the diameter of the dispersed phase is $<10\text{ nm}$ s $\ll 1\text{ nm}$ with a homogeneous system and the colour of the solution produced is different from the dispersed phase colour.

3.1. C-Dots Characterization

C-Dots which have been dispersed in distilled water with several variations of ratio are compared with distilled water as blank, then analysed qualitatively using UV lamps with a wavelength of 366nm to determine the resulting of luminescence properties. The luminescence results under the UV lamp can be seen in Fig. 2.

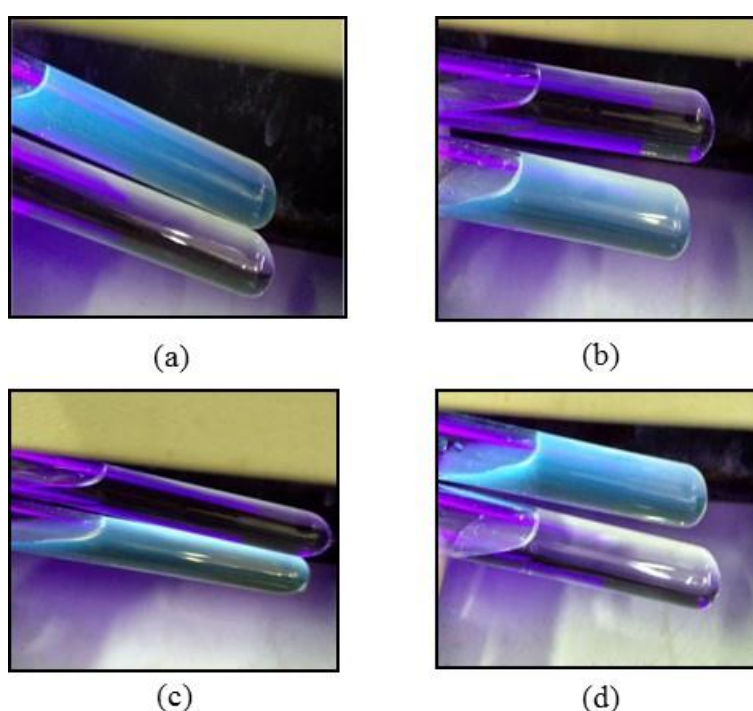


Figure 2. (a). Distilled water and C-Dots Ratio 4:1 (b) Distilled water and C-Dots Ratio 8:1 (c) Distilled water and C-Dots Ratio 12: (d) Distilled water and C-Dots Ratio 16:1.

The luminescence generated from each ratio is blue (the white blue) when illuminated by 366nm UV lamp while distilled water acts as a blank does not glow. The blue luminescence of UV light irradiation produces a blue fluoresced band [4]. Higher concentrated solution shows clearer illumination. It happens because more nano-sized particles are dispersed in the solution. The resulting luminescence colour is influenced by the microstructure of the dispersed C-Dots [7].

On the other hand, quantitative analysis using spectrophotometer shows that each dispersed C-Dots has a maximum absorption wavelength at 280.5nm. It indicates the presence of an organic functional group on the surface of C-Dots as shown in Fig. 3 [8].

The results of the FTIR characteristic test shown in Fig. 3 (a) It shows that there are typical functional groups that are owned by C-Dots. In the wave number of 3423.65 cm^{-1} , there is an -OH functional group with an absorption band area range of $3300\text{ to }3600\text{ cm}^{-1}$ and overlapping with NH functional groups with absorption band ranges between $3300\text{--}3500\text{ cm}^{-1}$. In the wave number of 2922.16 cm^{-1} , there is a C-H functional group with a range of absorption bands between $2850\text{ to }3000\text{ cm}^{-1}$. In the wave number of 1573.91 cm^{-1} , there is a functional group C=C with a range of absorption bands between $1450\text{--}1600\text{ cm}^{-1}$. In the wave number of 1089.78 cm^{-1} , there is a CO group with a range of absorption

bands between 1050 to 1200 cm^{-1} and overlapping with CN functional groups with a range of absorption bands between 1000 and 1250 cm^{-1} and in the wave number of 677,01 it indicates the presence of NH_2 and NH groups with a band area of absorption area between 660 to 900 cm^{-1} . The same thing has been done in previous research by Jelinek [6] using the same method and shown in Fig. 3(b). The results of FTIR characterization of C-Dots in this research shows the same results as Jelinek [6] research which shows the presence of an organic functional group in C-Dots are -OH , N-H , C-H , C=C , and C-O .

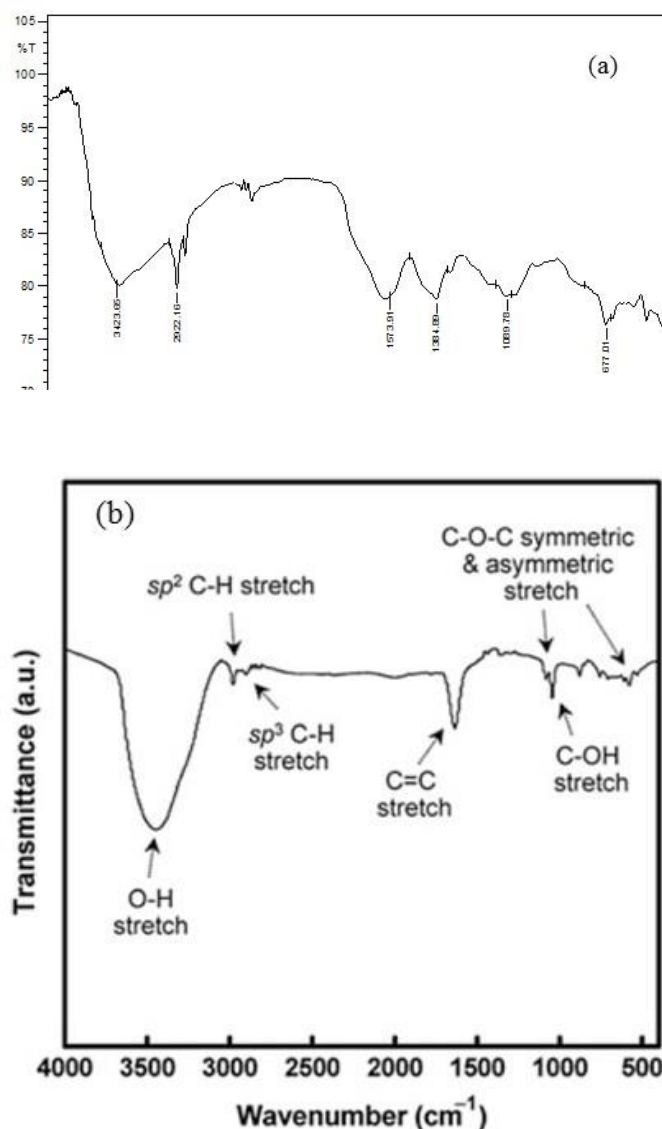


Figure 3. (a) FTIR analysis result of C-Dots Ratio 4:1(gram of C-Dots/1 liter of Dye Solution), (b) FTIR analysis result of C-Dots [6].

TEM (Transmission Electron Microscope) analysis is carried out at the Research Center for Nanoscience and Nanotechnology (PPNN), Bandung Institute of Technology (ITB). The purpose of the analysis is to determine the particle size inside the C-Dots. This tool has the ability to measure particles below 100nm with maximum magnification reaching 600,000 times. In additions this tool has the ability to take high-resolution images. The results of TEM analysis can be seen in Fig. 4.

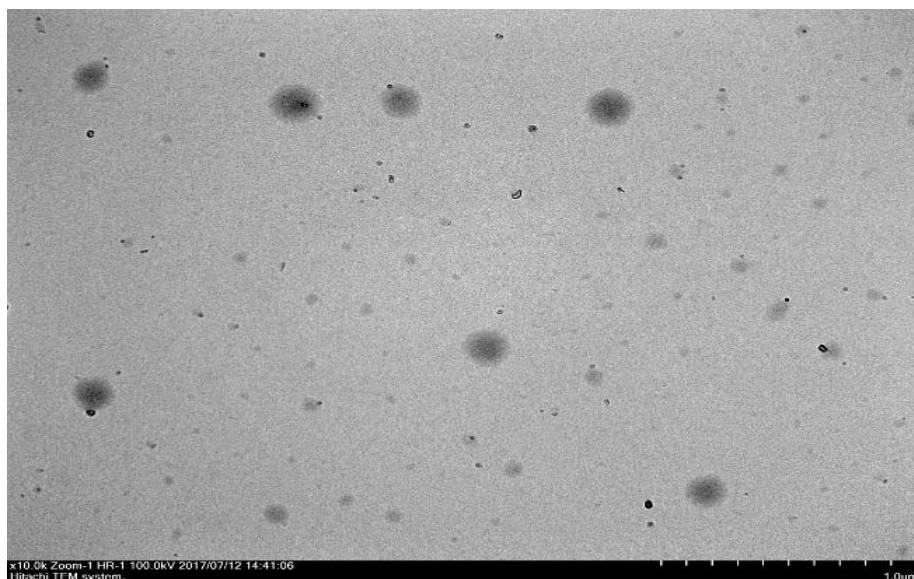
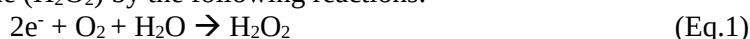


Figure 4. TEM Analysis of C-Dots Ratio 4:1 (g/L) 10.000x.

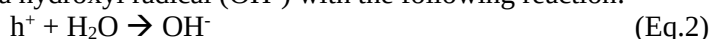
Fig. 4 shows the results of TEM measurements with 10.000x magnification, obtained the largest particle size of 30nm and the smallest size is 14nm. That result explains the successful of C-Dots productions using microwave method.

3.2. Performance Test of C-Dots

The C-Dots performance test was performed on the Skycion Yellow HE-4R solution with a concentration of 10 ppm. The degradation process was performed under visible light lamp (40 Watt wolfram lamp) for 7 hours then silenced for 24 hours. The visible light as a source of photons will be absorbed by carbon nanodots (C-Dots). The photons will make the electrons move from low energy levels to higher energy levels. The electrons will react with O₂ to form oxygen-free (Superoxide) free radicals and produce hydrogen peroxide (H₂O₂) by the following reactions:



In addition, this process also produces a hydroxyl radical (OH⁻) with the following reaction:



Free radicals that produced have a high potential to oxidize organic substances to produce H₂O and CO₂. The reduction and oxidation reactions that occurred causing degradation of the synthetic dyes and decomposed into water and CO₂ gas. C-Dots act as free-radical producing mediums such as super oxides and hydroxyl radicals that can decompose dyes with a relatively short time.

Fig. 5 shows the relation between absorbance and wavelength. It can be seen the effect of wavelength to the absorbance of dye solutions. The Skycion Yellow HE 4R of 10 ppm concentration having the highest absorbance around 0.015 at wavelength 700nm. Based on this results, the wavelength 700nm chosen as an optimum wavelength to determine the effect of adding C-Dots on Skycion Yellow H- 4R solution. Fig. 5 explains that adding C-Dots into Skycion Yellow HE-4R solution can reduce the absorbance of dye solution. At wavelength 700nm, the ratio of 4:1 (w/v) decrease the absorbance to 0.0044, it means that variation shows 70.67% degradation effectivity of azo dye solution. Comparing to others variations, it can be seen clearly that the increasing of C-Dots concentration shows higher absorbance which explain higher azo dye concentration. As the C-Dots ratio increased more particles were dispersed in the water, thereby accelerating the process of aggregation. Aggregations that occurred causing C-Dots that has size <10nm trapped within the aggregate, which may inhibit the degradation process.

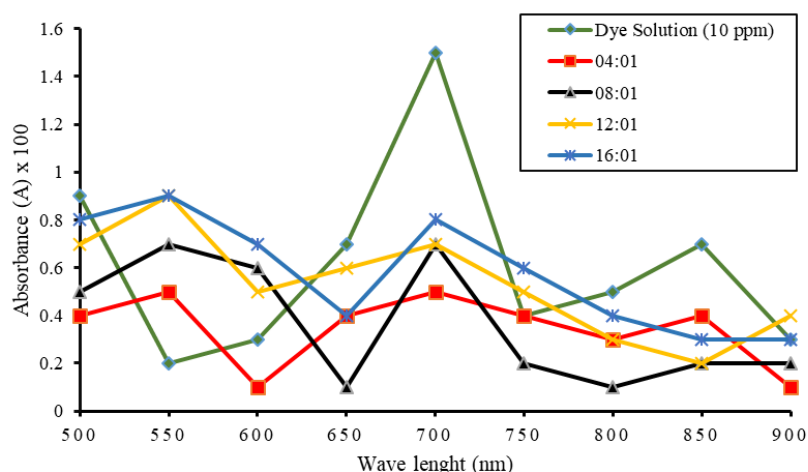


Figure 5. Relationship between wavelength to absorbance with 24 hours aging time.

Besides the decreasing of absorbance solutions, the effectivity of C-Dots on photo catalyst degradation of the azo dye solution can determine by COD parameter. Effect of C-Dots addition to COD shown in Fig. 6.

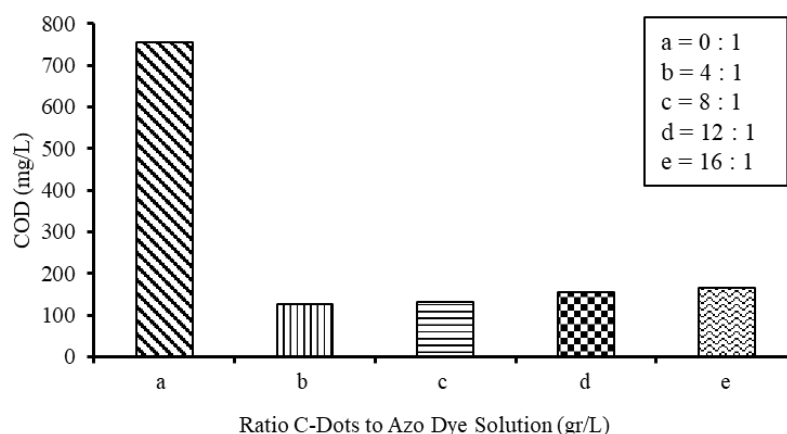


Figure 6. Relation Between C-Dots-Azo Dye Solution Ratio to COD in 24 Hours.

Fig. 6 shows the decreasing of COD after the addition of C-Dots at various ratio. The highest decreasing of COD occurred at 4:1 (w/v) ratio with effectivity 84.72%. This happened because the nature of photo catalyst in C-Dots. Photo catalyst reaction will occur and will take place when there is visible light [9].

4. Conclusion

Fluorescent carbon nanoparticle was obtained by microwave assisted methods after delignification and carbonation of water hyacinth. The light brownish yellow supernatant was collected that shows blue fluorescence under UV exposure. C-Dots with ratio 4:1 (gram C-Dots to liter of textile's waste water) shows the highest absorbance reduction on the azo dye, Skycion Yellow HE 4R, 10 ppm at wavelength 700nm with effectivity around 70.67% and decrease the COD with effectivity 84.72%. To conclude, C-Dots produced from Water Hyacinth has high effectivity to degrade azo dyes in textile waste water.

Acknowledgements

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